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STRUCTURE OF ALUMINUM HYDROXIDE POWDERS OBTAINED AS A BYPRODUCT OF HYDROGEN FUEL PRODUCTION

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The structure of aluminum hydroxide powders obtained as byproducts of hydrogen fuel production was investigated. One of the main initial components comprised aluminum-magnesium chips with 0.6, 6 and 12 wt.% magnesium. The phase composition and morphology of the powder particles were studied by x-ray phase and petrographic analysis. It was determined that the aluminum hydroxide powder obtained holds promise for obtaining corundum ceramic.

Key words: hydroxide, structure, composition, bayerite, gibbsite.

Aluminum hydroxide is formed as a byproduct during the operation of a hydrogen generator [1]. It is formed as a result of the action of a water solution of sodium hydroxide on aluminum (powder, chips) inside the cartridge of the hydrogen generator according to the following chemical reaction:

$$4Al + 3NaOH + 6H_2O = Al(OH)_3\downarrow + 3NaAlO_2 + 6H_2\uparrow. \quad (1)$$

The hydrogen released is used for its intended purpose as fuel, while the aluminum hydroxide is a byproduct of the work cycle of the hydrogen generator that must be used in order to lower the cost of the hydrogen produced.

From our point of view the reaction (1), as a result of which highly efficient fuel (hydrogen) is obtained, can be regarded as a novel technological approach to obtaining together with environmentally clean fuel (hydrogen) ultradisperse aluminum oxide powder. Ultradisperse aluminum oxide powder is obtained as a result of roasting aluminum oxide powder in ambient air. It should be noted that by using as the initial reaction product not pure aluminum but rather its alloy with strictly controlled content of alloying additives we obtain ultradisperse aluminum oxide powders in which the alloying additive is distributed uniformly (at the molecular level) over the entire volume of the powder. This technological expedient for obtaining high-quality ultradisperse powders, which is described in the current technical literature, has been termed the method of chemical dispersal [2, 3].

The aim of the present work is to study the structure of aluminum hydroxide powders, obtained as a result of the operation of a hydrogen generator, in order to evaluate the possibility of obtaining high-quality ultradisperse aluminum oxide powders from them.

The initial reaction products were aluminum-magnesium chips with 0.6, 6 and 12 wt.% magnesium and a concentrated water solution of sodium hydroxide. Three types of aluminum hydroxide powders were obtained by conducting the process: sample No. 1 ($Al–Mg_{0.6\%}$), No. 2 ($Al–Mg_{6\%}$) and No. 3 ($Al–Mg_{12\%}$). The structure of these powder samples was studied.

PETROGRAPHIC ANALYSIS OF THE PHASE COMPOSITION AND STRUCTURE OF ALUMINUM HYDROXIDE POWDERS

A Polam R-211 polarization microscope was used to perform petrographic analysis of powder samples by the method of immersion preparations in transmitted light [4]. The results of the analysis of aluminum hydroxide powders are presented in Table 1.

Sample No. 1. The main phase $Al(OH)_3$ is gibbsite, which crystallizes in the monoclinic system (refractive indices $N_g = 1.566$ and $N_m = 1.587$). The crystal habit of gibbsite is basalt tabular. The agglomerates are 4 – 8 μm long and

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TABLE 1. Results of Petrographic Analysis of Aluminum Hydroxide Powders

Sample No.	Main crystalline phase	System	Form of crystals	Refractive index	Crystal size, μm
1	Gibbsite	Monoclinic	Basaltic plates	$N_g = 1.566$ $N_m = 1.587$	< 1.0
2	Bayerite	Not determined	Flakes	$N_p = 1.583$	0.5 – 0.7
3	Bayerite	Not determined	Isometric hexa–octagonal crystals	$N_p = 1.583$	0.4 – 0.5

tenths of a micron to 6 μm wide. The amount of gibbsite on the area of the preparation is 80%, and the remaining 20% is comprised of flaky crystals smaller than 0.4 μm with refractive index $N_p = 1.555$. Their structure is close to the bayerite structure of aluminum hydroxide (bayerite $N_p = 1.583$), and they comprise a dense uniform mass, which does not disintegrate on grinding. Such crystals are joined into 6 – 10 μm spherulites. An impurity phase is also recorded (< 1%, occurring in the two main phases of aluminum hydroxide) — a continuous solid solution of $NaAlO_2$ in the complex hydroxide NaMgAlOH. In this phase the refractive index is lower than for $NaAlO_2$ ($N_g < 1.558$), and its composition changes from the center to the periphery of the particles. These particles form agglomerates with irregular (non-isometric) shape and 12 – 16 μm in linear size.

Sample No. 2. The main phase is bayerite with clearly expressed crystallization ($N_p = 1.583$). The crystals are flaky with 0.5 – 0.7 μm flakes. They are joined into isometric porous spherulites 15 – 25 μm in size. A solid substitution solution of Mg^{2+} in $Al(OH)_2$ with refractive index $N_p < 1.534$ is present along the boundaries of the flakes in agglomerates. The distribution of this phase between the bayerite flakes is uniform. The impurity phase $NaAlO_2$ was not found.

Sample No. 3. The particles in the powder composition have a layered structure. Aluminum alloy (20 – 25%) which has not reacted with the sodium hydroxide solution lies at the center and forms the core (10 – 12 μm), coated with a thin layer (1.5 – 6 μm) of amorphous boehmite (12 – 15%). The amorphous phase is covered with a layer of aluminum hydroxide (20 – 60 μm) in the form of bayerite (40 – 50%). The bayerite crystals are isometric in shape with rectilinear crystallographic faces. These are hexa-octagons 0.4 – 0.5 μm in size. An amorphous hydrate phase of precious spinel $(Al_2O_3 \cdot MgO) \cdot nH_2O$ (10 – 18%) is adsorbed on the boundaries of the rectilinear bayerite faces. The presence of the impurity phase $NaAlO_2$ (4%) was recorded. It is comprised of crystals in form of short prisms 4 – 8 μm in width and 8 – 12 μm in length.

It can be concluded on the basis of the petrographic analysis of the samples of mixed hydroxide powders that the main crystalline phases of aluminum hydroxide which are formed in a reaction of an aluminum alloy with sodium hydroxide are gibbsite and bayerite.

X-RAY PHASE ANALYSIS OF SAMPLES OF ALUMINUM HYDROXIDE POWDERS

X-ray phase analysis was performed with a DRON-3 diffractometer by the standard procedure [5].

Sample No. 1. The predominant phase is gibbsite. In addition, bayerite and sodium aluminate in the â-modification are identified in small quantities in this sample. Traces of a hydrate of precious spinel MgAlOH are also observed. It should also be noted that aside from the crystalline phases this sample contains an amorphous material of unknown composition. This material could be an embryonic phase $MgAl_2O_4$ at the initial stage of crystallization.

Sample No. 2. Bayerite and the complex hydroxide NaAlMgOH were identified in the powder sample. Two phases differing by the crystal lattice periods are present in this hydroxide. The lattice periods are $a = 0.8086$ nm and $a = 0.8068$ nm. These values suggest that the first phase is a solid solution of MgOH in NaAlMgOH and the second a solid solution of $Al(OH)_3$ in NaAlMgOH. Both phases are present in the same amounts. The bayerite content is a factor of about 7 higher than the total amount of these phases.

Sample No. 3. The complex hydroxide NaAlMgOH is recorded as the predominant phase. It is represented by two phases with different crystal lattice periods. The lattice parameter is 0.8080 nm in the first phase and 0.8028 nm in the second. The content of the first phase is a factor of 2 higher than that of the second. In addition, it should be noted that

TABLE 2. Results of x-ray Phase Analysis of Aluminum Hydroxide Powders

Sample No.	Crystalline phase	Crystalline phase content, vol.%	RCS,* nm
1	Gibbsite	95	< 100
	Bayerite	3	40
	$NaAlO_2$	0.5	50
	MgAlOH	1.5	45
2	Bayerite	63	< 100
	NaAlMgOH	37	50
3	NaAlMgOH	85	70
	Gibbsite	15	< 100

* RCS) size of the region of coherent scattering.

gibbsite is present in the material; its content is lower than that of the main phase by a factor of about 6.

Analysis of the data obtained shows that increasing the magnesium fraction (from 6 to 12 wt.%) in the initial Al–Mg alloy necessarily increases the yield of complex hydroxides.

CONCLUSIONS

It can be concluded on the basis of these studies that gibbsite is the predominant phase in aluminum hydroxide powder (sample No. 1).

Aluminum hydroxide powder (sample No. 2) contains several crystalline phases: bayerite and a complex hydroxide, whose composition can be described by the formula NaAlMgOH.

Depending on the method of analysis used either bayerite or the complex hydroxide NaAlMgOH is the predominant phase in aluminum hydroxide powder (sample No. 3). In this case petrographic analysis and XPA are at variance with one another. It seems to us that it is not entirely correct to attribute this discrepancy to random error.

Thus, the aluminum hydroxide powder obtained is a promising material for obtaining corundum ceramic.

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